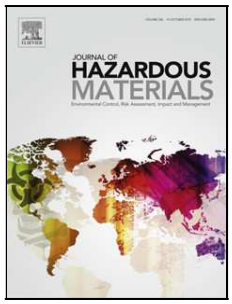

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Assessment of Nanoparticles Release into the Environment during Drilling of Carbon Nanotubes/ Epoxy and Carbon Nanofibres/Epoxy Nanocomposites

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Highlights

- Real-time nanoparticle release quantification from life-cycle scenario
- Particle number concentration, size distribution and mass concentration of particles released
- Hazardous nanoparticles released significantly exceed recommended exposure limits
- Comparison and effect of carbon nanofibers and nanotubes to neat epoxy matrix
- Demonstrated nanoparticle release methodology without background particles within detection limits of the CPC

Abstract

The risk assessment, exposure and understanding of the release of embedded carbon nanotubes (CNTs) and carbon nanofibers (CNFs) from commercial high performance composites during machining processes is yet to be fully evaluated and quantified. In this study, CNTs and CNFs were dispersed in epoxy matrix through calendaring process to form nanocomposites. The automated drilling was carried out in a specially designed drilling chamber that allowed elimination of background noise from the measurements. Emission measurements were taken using condensed particle counter (CPC), scanning mobility particle sizer (SMPS) and DMS50 Fast Particulate Size Spectrometer. In comparison to the neat epoxy, the study results revealed that the nano-filled samples produced an increase of 102% and 227% for the EP/CNF and EP/CNT sample respectively in average particle number concentration emission. The particle mass concentration indicated that the EP/CNT and EP/CNF samples released demands a vital new perspective on CNTs and CNFs embedded within nanocomposite materials to be considered and evaluated for occupational exposure assessment. Importantly, the increased concentration observed at 10nm aerosol particle sizes measurements strongly suggest that there are independent CNTs being released at this range.

Keywords: Nanoparticle release, carbon nanotubes, carbon nanofibers, drilling emissions

1. Introduction

The recent developments in understanding and improved manufacturing techniques of nanoparticles have rapidly introduced engineering nanomaterials (ENMs) across the commercial industry. The ability to incorporate nanofillers within polymers has permitted extensive research and progress in targeting specific material properties with great control and precision. This capacity has shown that epoxy based nanocomposite materials for uses in high-performance lightweight applications where carbon nanotubes (CNTs) and carbon nanofibers (CNFs provide significant enhancements in properties: mechanical [1,2], electrical [3,4], thermal [5,6], and fire retardant [7, 8] properties. As a result, worldwide CNT production capacity of CNT's has increased at least 10-fold since 2006 [9] and according to a report by Global Industry Analysts Inc. [10], the global market for nanofibres is projected to reach US$1 billion by 2020.

Despite the beneficial material properties of CNTs and CNFs, the nanofillers have shown conceivable health risks and toxicity to humans and the environment. The use and introduction of these materials into the workplace can be hazardous when human exposure is concerned [11]. Studies have validated that certain concentrations of CNT exposure has shown to induce cytotoxicity and apoptosis [12, 13], genotoxicity [14, 15], systemic immune function alterations [16] and pulmonary damage, inflammation and granuloma lesions [17-19]. Review papers have been released in an attempt to quantify various CNT attributes to the level of toxicity. Many studies with varied types of CNTs, different evaluation methods and different exposure conditions have shown conflicting results as presented by Liu et al., [19]. Consequently, we are still, at present, unable to classify and gauge exact level of toxicity factors such as size, shape, purity and functionalisation to CNT toxicity [21]. However, in the findings from Aschberger et al. [22], studies suggest that chronic occupational inhalation; especially during activities involving high CNT release and uncontrolled exposure are the main risks for humans.

Equally, CNFs are increasingly being investigated for toxicity. Studies have shown inhalation or exposure to a varied concentration of CNFs to cause respiratory tract and pulmonary inflammation [23-25], DNA damage [26] cell proliferation inhibition and cell death [27]. Despite the evidence of toxicity and widespread use of CNFs, most studies have investigated CNTs. However, additional to offering economic benefits over CNTs with a better cost to strength ratio, some studies have suggested that CNFs show less toxicity than CNT's [23, 28, 29].

Already established within industry and it is acknowledged that throughout its lifecycle, epoxy nanocomposites will undergo drilling during assembly operations where the nanofillers could

unintentionally be released and exposed to workers and/or consumers. An Airbus A350 will undergo 16000 holes drilled per composite wing set [30]. Various studies have considered nanoparticle release due to various mechanical processes such as cutting [31], abrasion [32], sanding [33], sawing [34] and drilling [35] just to name a few. However, there is still a lack of understanding and being able to link the release of the embedded hazardous nanoparticles to exposure [36]. Kuhlbusch et al. [37] reviewed the current studies in nanoparticle exposure in workplaces and found nanomaterials of <100nm to be released in only a few cases, but a regular release of >300nm was observed in another review. Froggett et al. [38] summarised the existing release studies from mechanical scenarios, highlighting the current gap in knowledge with only 54 publications covering the release from solid non-food nanocomposites. From the experimental studies, 96% demonstrated release of nanoscale debris from the nanocomposites [38]. Both review articles agreed on a lack of systematic harmonized methods to compare the results and identified the need of a standardised method to test or characterise the release and exposure of nanoparticles from nanomaterials during a lifecycle scenario.

Studies in the open literature have investigated various life cycle mechanical processes which generate airborne material release which could potentially expose workers to the nanoparticles. Drilling is a fundamental and significant machining process used during assembly operations. In a review on the effects of drilling on nanocomposites, three studies were identified to have investigated the release of nanoparticles from nanocomposite materials [39, 40]. All three studies demonstrated nanoparticles to be released. In one of the studies by [41], nanosilica filled nanocomposites demonstrated 56 times on the nano-emissions than conventional fibre reinforced composites. In a study by Bello et al. [42], collections of CNTs were revealed in the emissions after drilling on CNT-alumina and CNT-carbon nanocomposites. With a similar study using cutting, drilling demonstrated significant differences and an increase in overall nanoparticle release [43]. In contrast, another study by Sachse et al. [41] displayed a reduction in the number of airborne nanoparticles by a factor of 20 when nanoclays were added to neat PA6. However, the concentration of deposited nanoparticles doubled for the nanocomposite.

Along accessing the cost to performance ratio and with a better understanding or reduction of toxicity introduced from nanocomposites, materials can be manufactured to be safer by design. Data collected for nanoparticle release can be used towards developing materials which will reduce or potentially not release the toxic nanoparticles and hence, safer for workers and consumers. It is now recognised that safer by design allows bridging the gap between the rapid developments in nanotechnology and nanosafety assessment [44].

The aim of this study is therefore to investigate and characterise the effect CNTs and CNFs have on nanoparticle release from industrial nanocomposites due to drilling. The studies on drilling on nanocomposites thus far have revealed that nanoparticle fillers do influence nanoparticle emissions but have been unable to determine the risk and exposure. Little is known on the full potentially hazardous effect drilling polymer nanocomposites reinforced with CNTs and CNFs have on nanoparticle release. This study thus examines industrial used epoxy nanocomposites filled with CNTS and CNFs. The sampling and methodology undertaken were developed as a part of a controlled drilling protocol within the European Commission Life project named Simulation of the release of nanomaterials from consumer products for environmental exposure assessment (SIRENA, Pr. No. LIFE 11 ENV/ES/596) [45], with the sole intention of testing these nanocomposites for nanoparticle release into the environment from the composite matrix system during machining processes. The study is part of a wider project aimed at developing a standardized test method for the release of nanoparticles from industrial nanomaterials at various stages of material development.

2. Experimental Methods

2.1 Materials and Fabrication

A commercially available bi-component epoxy resin system MVR444R from CYTEK Solvay Group (former ACG) was reinforced with unmodified multi-walled carbon nanotubes with an average diameter of 10-15 nm (Multi-walled Graphistrength C100 from ARKEMA Inc.) and unmodified carbon nanofibres with an average fibre diameter of 100 nm (PYROGRAF PR24-XT-LHT from APPLIED SCIENCES INC) due to their electrical properties. A concentration of 2 wt. % of CNT and 2 wt. % of CNF were dispersed in the epoxy matrix through calendaring using a commercially available laboratory scale three-roll mill (EXAKT 80E, EXAKT Technologies Inc.) and cured in an oven process. The process involves employing repeated high shear stresses generated by the gap within the three rollers to disperse the CNTs and CNFs homogeneously in the epoxy. Manufactured sample measuring 70 mm x 45 mm x 5mm were prepared for the drilling tests. Corresponding samples of 90 mm x 70 mm x 2mm sample size were also fabricated for the standard DC resistance or conductance testing of moderately conductive materials using ASTM D4496 [46] and for insulating materials ASTM D257 [47].

2.2 Nanoparticle Release Setup – Automated Drilling Method, Instrumentation and Measurement Procedure

The materials were tested using a purpose built controlled test chamber that allows direct measurement of nanoparticles emitted during drilling. The process is developed and initiated by the

SIRENA Life project –an acronym for Simulation of the Release of Nanomaterials from Consumer Products for Environmental Exposure Assessment [45]. This process is designed to simulate mechanical drilling on nanocomposite materials and is continued work from the NEPHH project study [40]. Building on the NEPHH project, the chamber designed for present study is capable of achieving a clean environment monitored using a CPC, importantly removing all background noise or interference on the measurement of number concentration and particle size distribution. This approach differs from the Nanoparticle Emission Assessment Technique (NEAT) in that it initiates by investigating the nanoparticle release related to background data [48] instead of a clean environment. The data collected in our present setup however, is a true representation of the particles released solely from the material. Discounting the background data allows for a complete understanding of any hazards released from the materials which can be directly linked as an unconditional maximum exposure assessment.

In our study, once the chamber was cleared of any particles, the drilling studies were carried out by drilling across the width of the sample resulting in eight separate holes and bearing time duration of 3 minutes. The eight holes drilled per sample were repeated three times to get an average of the particle number concentration released.

Based on previous studies [35, 39-42] carried out on nanocomposite drilling, a standard Dremel 4000 drilling tool with an industrial standard stainless steel 3.5mm twist drill bit was used at 10000 rpm with a feed rate of 78 mm/min. The setup uses an automated drilling assembly operated externally to the chamber to permit a repeatable and controlled environment within the chamber as shown on Figure 1.

Figure 1

The closed steel chamber has dimensions of 740 mm x 550 mm x 590mm, and therefore a total inner volume of 0.240m^3. It is designed to assure a closed environment to simulate an appropriate volume around the drill and minimising electrostatic attraction to the surfaces. To quantify only the particles released from the sample, the chamber was initially cleared of particles through an inflow of clean air with the use of TSI 99.97% retention HEPA Capsule Filters. A separate capsule was constructed around the drill with separate air flow to avoid any interference of the drilling fumes on the particle number concentration within the capsule. The clean air system using the HEPA Capsule filters was

capable of producing a particle number concentration reading within the chamber of 0 particles/cm^3 with false background counts <0.01 particles/cm^3, as measured using a TSI Environmental Particle Counter (CPC) model 3783 at a flow rate of 0.6 LPM, particle range of 7-3000 nm and concentration range of 0-106 particles/cm3 and ±10% at 10^6 particles/cm^3. The level of background noise is therefore well within the ISO 14644-1 cleanroom standard for particles ≥0.1 µm of 10 particles/cm^3.

An outlet channel is placed adjacent to the test specimen for the nanoparticle release equipment readings. A sampling grid for post-test analysis and characterization of the airborne particles was placed next the test specimen with a slight suction to attract and prevent particles from detaching away from the grid. An additional sampling tray was positioned below the test specimen for collection of the deposited particles for further post-test analysis.

The scanning mobility particle sizer (SMPS) used for the study is a TSI 3080 Electrostatic Classifier utilizing a nano Differential Mobility Analyser (DMA) with 99 distinct particle diameters within a particle range of 4.61 -156.8 nm and a flow rate of 0.31 lpm. The principle of the Model 3080 Electrostatic Classifier with the DMA is based on the monotonic relationship between electrical mobility and particle size with singly charged particles. The aerosol particles go through a process of bipolar charging or “neutralization” and are then classified with the differential mobility analyser and then measured by a Condensation Particle Counter. The given particle size distribution is therefore corresponding to the electrical mobility diameter. In addition, separate repeated runs were carried out using a Cambustion DMS50 Fast Particle Size Spectrometer with a 1 second sampling period, inlet flow rate of 6lpm, with 34 distinct particle diameters of size range between 4.87nm – 562.34nm was used for the particle size distribution. The DMS50 utilizes a unipolar corona charger placing positive charges on each particle which are then classified along electrometer detectors based on mobility and hence particle size. The charge is conducted via an electrometer amplifier whose output indicates the flux of particles giving the particle concentration at that given particle size. Since the classification of particles according to their differing electrical mobility takes place in parallel (rather than in series as in the SMPS) the DMS50 can offer the faster sampled particle size distribution. This allowed for a size distribution every second compared to the SMPS of 45s period (followed by 10s for the classifier to regenerate to its initial voltage and 5s to start the size distribution again) and therefore an accurate representation of the particles being released from the sample in a given time. Particles released (drill cuttings) or deposited from the drilling process were captured using the sampling tray as shown in Figure 1 and Figure 2 to be analysed with an SEM.

Figure 2

The SMPS uses the assumption of spherical particles. Hence, from the diameters of the particle size distribution measured, and the material density of the nanocomposites, the particle mass size distribution can be estimated. The assumed constant material density for the three nancomposties are: EP= 1.24 g/cm^3, EP/CNT = 1.20 g/cm^3 and EP/CNF= 1.14 g/cm^3.

Both Zeiss EVO LS10 Variable Pressure Scanning Electron Microscope and an SEM/EDX (FEI Quanta 200F) with a beam current of 208 μA and voltage of 10 kV were used for present study and cross-checked using an electron probe microanalyser (EPMA) JEOL JXA-8621MX, with beam current of 30 nA and voltage of 15 kV. SEM samples of the materials were prepared using sputter coating of an ultra-thin coating of gold to minimize charging. A sampling tray placed immediately below the drilling set up in the chamber (see Figure 1) was used to collect debris removed from the nanocomposites during the drilling operation.

2.3 Conductivity Testing

The materials were tested in accordance with direct current (DC) resistance or conduce of moderately conductive materials and of insulating materials test standards ASTM D-4496 and ASTM D-257 respectively, to demonstrate significant improvements in surface and volume conductivity respectively [46,47].

3. Results and Discussion

3.1 Conductivity Properties

To validate and complement the references on enhanced properties achieved with the use of CNTs and CNFs, the materials were testing for direct current (DC) conductivity measurements. The results are illustrated on Figure 3.

Figure 3

With the chosen 2 wt. % of both carbon nanofillers, the surface and volume conductivity of the nanocomposite material significantly improved by up to a factor of 8. A comparable magnitude of improvement is in literature with the same matrix-filler combination [4, 49]. The same weight concentration presented the CNTs with a superior performance than the CNFs.

3.2 Filler Effect on Particle Number Concentration

The epoxy based nanocomposite samples underwent the replicated drilling setup as described in sub chapter 2.2. In comparison to the neat Epoxy sample, the introduction of CNTs and CNFs significantly effect the nanoparticle release from the drilling process.

A graphical representation of the CPC particle number concentration averages from the repeated runs on the samples is displayed in Figure 4. Across the duration of 4 minutes, 8 peaks exemplify the 8 holes drilled before the 1 minute of post drilling. For each individual hole, the peak concentration introduced into the chamber is observed to be split into two, revealing the drill entering and withdrawing the sample. Importantly, all three of the samples can be seen to introduce a high concentration of nanoparticles into the chamber, including the neat epoxy sample. Upon completion of the drilling of 8 holes, the concentration relatively stabilize for the final 1 minute of data sampling. Similarly, the concentration remains relatively linear between each hole being drilled. The mechanical drilling therefore generate a substantial quantity of nanoparticles into the environment, which then quickly disperse, but remain airborne.

Figure 4

The substantial particle number concentration from the epoxy-based samples surpassed the CPC concentration limit of 1 x10^7 #/cm^3 on numerous instances. During the first drilling run of the neat epoxy, the emissions exceeded this limit on two occasions. The EP/CNF and EP/CNT samples both surpassed the limit on three occasions. The averages plot in Figure 4 illustrate the two nano-reinforced samples evidently produced a more consistently high peak towards the limit of the CPC compared to the neat epoxy sample. The data of the three samples clearly illustrate the augmenting effect of the carbon nano-fillers on the particle number concentration. The neat epoxy sample exhibited a concentration lower than the reinforced samples for virtually the entire four minutes. The EP/CNF sample produced noticeably higher concentration in relation to the neat epoxy, but lower than the EP/CNT sample. Whilst producing the highest concentration and peaks during the drilling, the CNT sample furthermore demonstrated the highest concentration at the end of the four

minute examining period. The high number concentration introduced during the drilling disperse within the chamber but crucially remain airborne. The EP/CNT sample presented a particle number concentration remaining above 1x 10^6 #/cm^3 even after the drilling and 1 minute post drilling was concluded. Additionally, as more holes were drilled on the EP/CNT, the relatively stable concentration between holes increased for the three samples. This advocates the induction and augmenting effect drilling has on nanoparticles from the samples.

Table 1

Since all three samples exceeded the maximum limits of the CPC measurement capability (i.e. 1x 10^7 #/cm^3), the samples produced the same peak particle number concentration in the numerical data representation in Table 1. The mean peak values are influenced and confined by the saturated CPC measurements (twice for EP and three times for the EP/CNT and EP/CNF samples) and are therefore only a lower bound representation. The high standard deviation and range demonstrate a level of randomness and uncertainty in the peak releases. Taking the saturated values into consideration, the EP/CNT and EP/CNF samples demonstrated a clear increase in particle number concentration during drilling peaks, between drilling and across the entire 4 minutes of sampling. From the numerical values, the EP/CNT reinforced sample exhibited the uppermost mean value over the 4 min of 1.48 x 10^6 #/cm^3 introduced into the chamber due to drilling. Furthermore, the EP/CNT sample demonstrated the largest concentration after 4 minutes of sampling (1.01 x 10^6 #/cm^3). In relation to the neat epoxy, the EP/CNF and EP/CNT produced an increase of nanoparticles of 102% and 227% in average over the 4 minutes when excluding the saturated values. Therefore, the carbon nanofillers studied led into increase on the emitted particle number concentration recorded.

3.3 Filler Effect on Particle Size Distribution

With a sampling period of 1 minute, an average of the 4 data sets from the SMPS across the 4 minutes for each sample is displayed in Figure 5. The three samples exhibited two distinct peaks on the SMPS. The smaller peak for the samples occurred at around 10nm, and a larger particle diameter peak between 20-30nm. The size distribution data illustrates minimal effect of the carbon nanofillers on new peak diameters in comparison to the epoxy sample. The reinforced samples displayed an increasing effect in magnitude on the particle number concentration although little difference in the

shift of particle diameters was observed. Nonetheless, two of the peak size distributions are indicated to be around the same particle diameters.

Figure 5

Since the increase in particle number concentration is at the same particle diameter denotes that the particles are matrix associated, and not the nanofillers independently. Any independent carbon nanofillers or matrix-filler embedding released from the samples would be expected to demonstrate a different peak in particle diameter from the neat epoxy sample. Evidenced from the SMPS data alone, the addition of the CNTs and CNFs can be established to affect the material particle number concentration, but is assumed not to release the fillers independently from the matrix or sample. Since the CNTs have a diameter of 10-15nm, the increased concentration observed at 10nm in Figure 5 may lead to the suspicion that this could be caused by independent CNT. However, for this hypothesis to be true, the peak would not be expected for the EP/CNF or EP sample e.g. CNF has 100nm diameter, and includes the assumption of the SMPS that the particles are of a spherical nature.

Further to the data collected on the SMPS, separate data was also gathered on the DMS50 for the particle size distribution. The size distribution at each second is displayed in a three-dimensional plot as shown for the EP/CNT reinforced sample in Figure 6. Note; the data is taken from a separate run to the CPC and SMPS data due to the required increased inflow rate.

Figure 6

As with the CPC data shown in Figure 4, the eight peak particle number concentrations introduced due to the drilling are visibly notable in the DMS50 data shown in Figure 6. The final two holes drilled revealed a reduced peak value in comparison with the previously drilled 6 holes on the same sample. The relatively constant concentration between each peak is seen to increase after each hole being drilled up until the 7th hole followed by a minimal decrease in concentration perceived during the 1-minute post-drilling. A less consistent peak particle number concentration was observed for the

EP/CNT sample with a standard deviation of 6.21 x10^6 #/cm^3 and coefficient of variation of 34%, compared to the CPC data with a standard deviation of 1.09 x10^6 #/cm^3 and coefficient of variation of 13%.

The peak particle number concentrations during the drilling of each hole are seen to be consistent in particle size distribution. Similar to the SMPS data shown in Figure 5, no particles are measured above 40 nm for the duration of the 4-minute sampling time. No change in size distribution from the peaks to the constant concentrations removes the prospect of agglomeration (below 562nm) of particles within the chamber after the 1 second sampling time. Considering the DMS50 data, if particle agglomeration were to happen it would have to occur instantaneously. The particles are however seen to rapidly disperse within the chamber.

The almost instantaneous particle size distribution permits an analysis on the peak concentrations at the moment of drilling. Figure 7 illustrates a two-dimensional particle size distribution plot of the largest peaks released from the three samples. A similar size distribution at distinctively different number concentrations is observed.

Figure 7

A common peak between 7-9nm for the three samples can be seen to be released from the drilling. As with the CPC and SMPS data shown in Figure 4 and Figure 5 respectively, the two nano-filled samples released a considerably higher number concentration. All three instruments used to quantify the released particles (CPC, SMPS & DMS50) demonstrate a harmonised increase in particle number concentration with the introduction of the CNTs and CNFs. The EP/CNT produced the highest concentration in all three instruments.

In contrast, the presence of the carbon nano-fillers can be seen to have a limited effect on the particle size distribution. All three of the samples displayed a peak concentration of released particles below 10 nm. But the size distribution of the nano reinforced samples can be seen to be relatively similar to the neat epoxy. It is bold to compare with other studies mainly due to the presence of background particles in other studies, however this trend can be seen to coincide with a study on Epoxy-CNT release due to Abrasion by Schlagenhauf et al. [32], where no additional particle size mode was observed with the introduction of the CNT nanofiller. Similarly, Wohlleben et al. [50],

concluded no influence of CNTs on the particle size distribution could be detected from POM/CNT nanocomposites due to abrasion. Nonetheless, the use of CNTs and CNFs as nanofillers in epoxy have both demonstrated improved mechanical properties such as fracture toughness, and influence friction coefficient and the wear rate of nanocomposites can be reduced significantly [51,52,53]. Furthermore, studies have found nanocomposites may exhibit inhomogeneity when a scale close to the nanofiller is considered and display more obscure behaviours than the neat matrix [32]. In contrast, an assumed brittle nature of the fracture causing the particle concentration increase does not justify no shift in the diameter of particle size distribution.

In comparison to the SMPS average over the 4minutes, the size distribution on the DMS50 sampled at 1 second is disparate as only one peak is visible. However, both plots indicate that none of the samples emitted any particles above 50 nm. The second peak in particle diameter in the particle size distribution from the SMPS data was not recorded on the DMS50. These disparate peaks seen on the two instruments introduce debateable deductions and effectiveness of instrumentations required for real-time data. Studies in the literature have experienced similar issues as reported by Njuguna and Sachse [44] who documented the limitations and deficiencies of current nano-sized aerosol measurement techniques. Although the two instruments both use electrical mobility measurements to classify the particle size distribution, the difference in sampling period could be the source of the varied results in real-time measurements during drilling. In summary, the SMPS data revealed minor differences on the particle size distribution compared to DMS50. Although the evidently greater particle number concentrations, the same particle diameters indicate a matrix association. A similar conclusion can be drawn from the DMS50 data. However, the two instruments displayed similar small diameters in the particle size distributions with a high percentage of the particles within 6-20 nm, and no significant concentration larger than 70 nm. The fillers therefore had minor effect on the particle size distribution.

3.4 Filler Effect on Mass Size Distribution

Since the drilling was conducted within a clean environment, all of the particles measured with the instrumentation is from the nanocomposite material. With the use of the SMPS and assuming the known density of the individual nanocomposites to be constant, the particle mass concentration can therefore be estimated. The data utilises the diameter of the particles measured using the SMPS.

Figure 8

The average mass concentration across the 4-minute sampling period for different particle size diameters is illustrated in Figure 8. The particle diameters with high particle number concentrations observed in the SMPS results on Figure 5 have adjusted due to the consequent mass increase of larger particles. Figure 8 displays a peak particle mass concentration at the same particle diameter for the three samples at around 30nm. As with the particle number concentration and particle size distribution, the carbon nanofillers still clearly demonstrate an augmenting effect in concentration, with the EP/CNT sample revealing the highest particle mass concentration between the three samples.

Various governing institutes have attempted to develop maximum exposure limits when concerning release of hazardous materials. The United States federal agency responsible for occupational related injuries and illness, the National Institute for Occupational Safety and Health (NIOSH), have published a report on the hazard and exposure assessment when working with independent CNTs and CNFs [54]. From the risk assessment conducted, NIOSH published recommended exposure limits (RELs) in relation to free CNT material. The estimated exposure concentration dosage associated with a 10% risk of adverse lung effects and above background for a slight or mild lung effects (grade 2 or higher) was given a maximum likelihood estimate of 1 to 44 μg / m^3 during an estimated working lifetime exposure concentration (8-hr TWA). However there is currently no exposure limit when considering CNTs or CNFs embedded within a nanocomposite. The addition of the nanofillers demonstrate a substantial nano-sized mass size distribution distinction to the neat epoxy sample and therefore open a new perspective for exposure assessment. The difference and 330% increase from neat epoxy to EP/CNT in total particle mass concentration observed and exhibited on Figure 8 is not to be compared to the RELs as no free standing CNTs or CNFs have been identified, but establishes a necessary new release exposure to be considered and evaluated.

3.5 Microscopy Studies on Deposited Particles

Debris collected in the chamber as shown in the schematic on Figure 1 was analysed using an SEM and EDX. An SEM image of the neat epoxy, EP/CNF and EP/CNT samples are displayed in Figure 9.

Figure 9

The SEM images on Figure 9 illustrate the material surfaces with a scale of 10µm. The SEM limitation was unable to identify free standing CNTs or CNFs, but dissimilarity between the materials can be seen. An EDX study was also performed on the samples and as expected, due to the nature of the epoxy matrix a high concentration of carbon was detected. The surfaces demonstrated different textures and morphologies revealing the material release variances. Diverse agglomerations of matrix fragments covered in nanoparticles are observed across the three materials. Critically, no independent CNTs or CNFs were established and therefore indicating that the CNTs and CNFs remain embedded within the epoxy matrix. Further studies are required to validate the absence of independent CNTs and CNFs. In comparison, TEM analysis of released particles from a study on epoxy-CNT nanocomposites by Schlagenhauf et al [32], revealed protruding CNTs, agglomerates of CNTs and also free standing CNTs were emitted due to abrasion. Other studies on release due to abrasion such as Wohlleben et al. [55] and Wohlleben et al. [50] on PU/CNT and POM/CNT respectively, found no release of CNTs from TEM analysis. A review on the release of CNTs from polymer nanocomposites by Schalgenhauf et al. [56] found the release of CNTs to be dependent on material and machining process. The review concluded that some materials, including epoxy, provided a better filler-matrix interface and dispersion, reducing or even preventing the release of CNTs.

4. Conclusions

Three epoxy based nanocomposites were fabricated with two different carbon nanofillers (CNTs and CNFs). The improved conductivity properties were demonstrated from the neat epoxy with the reinforced 2 wt.% CNFs and 2 wt.% CNTs. The samples tested, including the neat epoxy, revealed that nanoparticles were generated and released from the sample during the drilling process. It was established that all three samples emitted significant concentrations which surpassed the limits of the CPC instrument on several occasions during the drilling. In comparison to the neat epoxy sample, the EP/CNF and EP/CNT samples produced an increase during drilling, between drilling and a 102% and 227% respectively in average particle number concentration across the 4 minutes when excluding the saturated values. The particle mass concentration revealed a substantial increase with the addition of CNTs and CNFs in comparison to the neat epoxy. This diagnoses a vital new perspective on CNTs and CNFs embedded within nanocomposite materials to be considered and evaluated for occupational exposure assessment. Nonetheless, the data includes release of the
epoxy matrix and revealed no evidence of independently free standing CNTs or CNFs in the microscopy of the deposited particles. Importantly, the increased concentration observed at 10nm aerosol particle sizes measurements strongly suggest that there are independent CNTs being

released at this range. We are however unable to measure and validate beyond any reasonable doubt due to limitation of the current state of the art equipment techniques and methodology employed in this study and therefore warranting further research.

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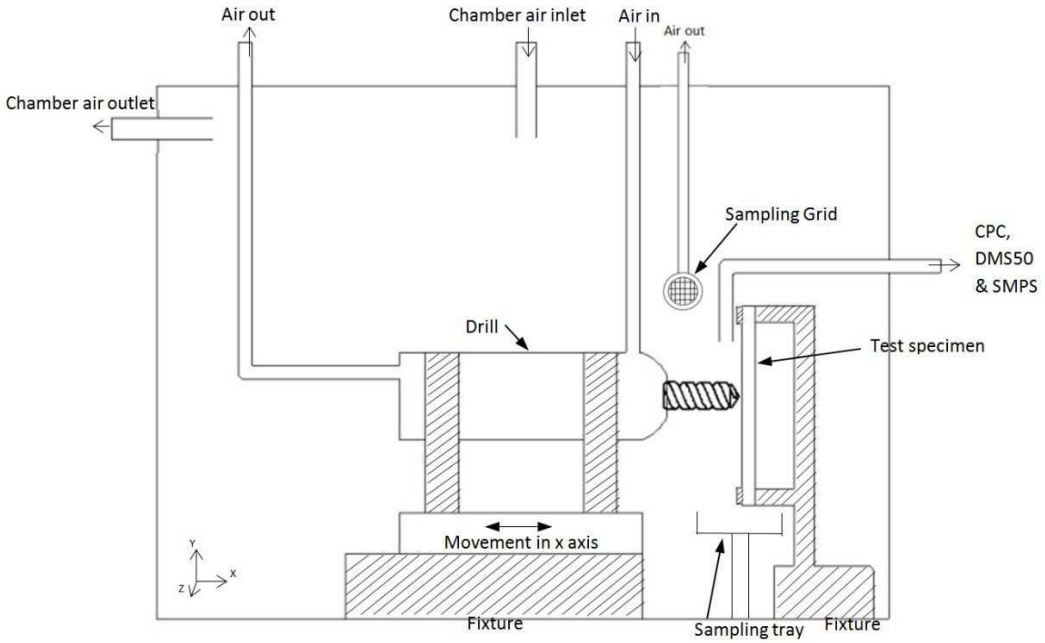

Figure 1: Schematic drawing of automated drilling setup within enclosed test chamber with cycled airflow to allow for a clean environment removing any background interference

Figure 2: Apparatus setup of drilling within enclosed chamber with front window panel removed and side door open

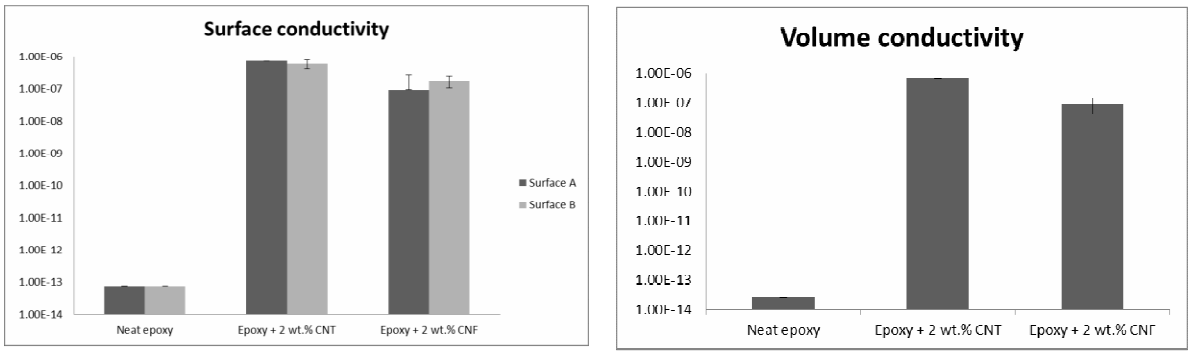

Figure 3: Surface and Volume DC conductivity measurements for EP/CNT and EP/CNF compared to neat EP

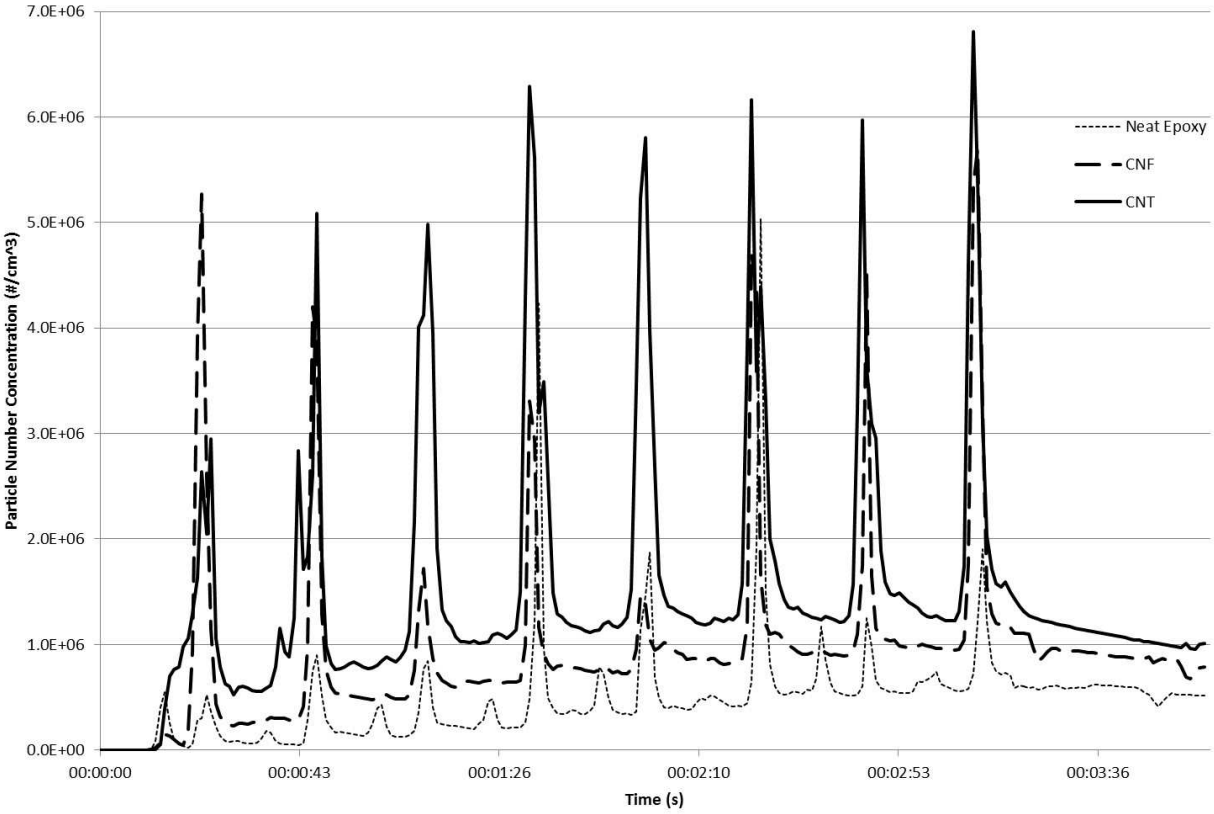

Figure 4: Particle number concentration averages of nanoparticles introduced from epoxy-based samples (measured using CPC)

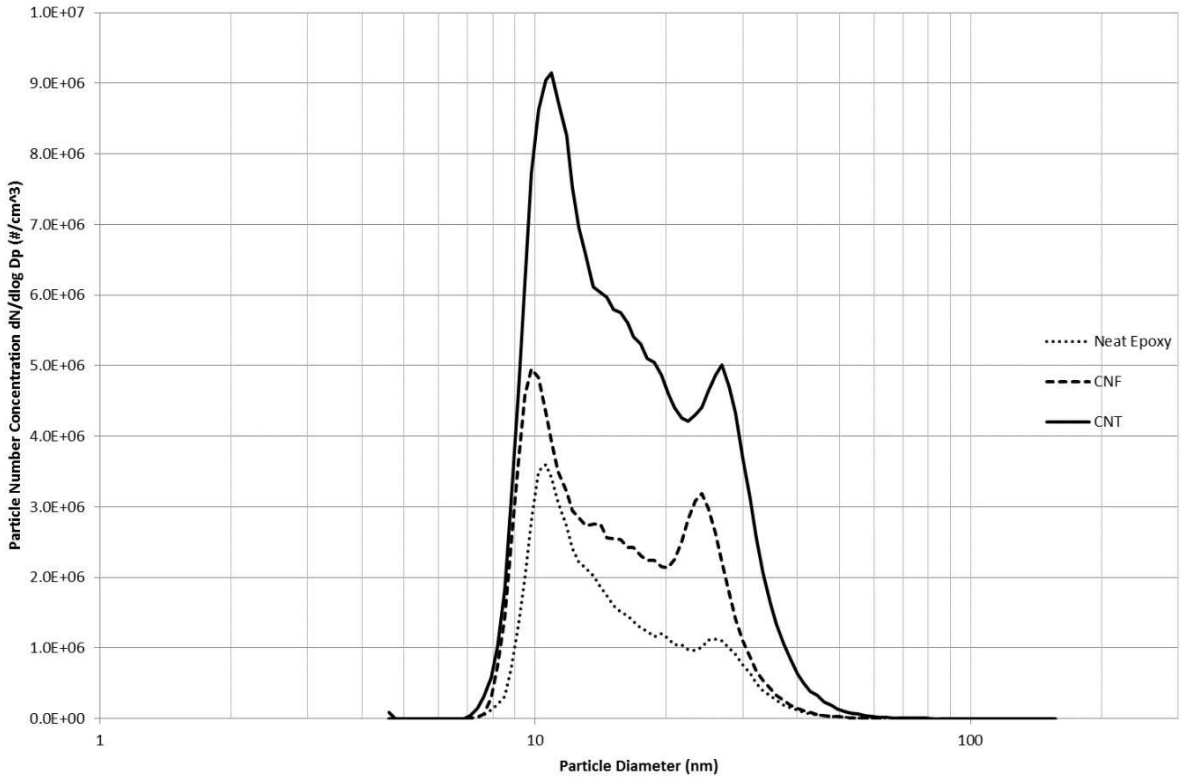

Figure 5: Average particle size distribution measured using SMPS of Epoxy-based nanocomposites

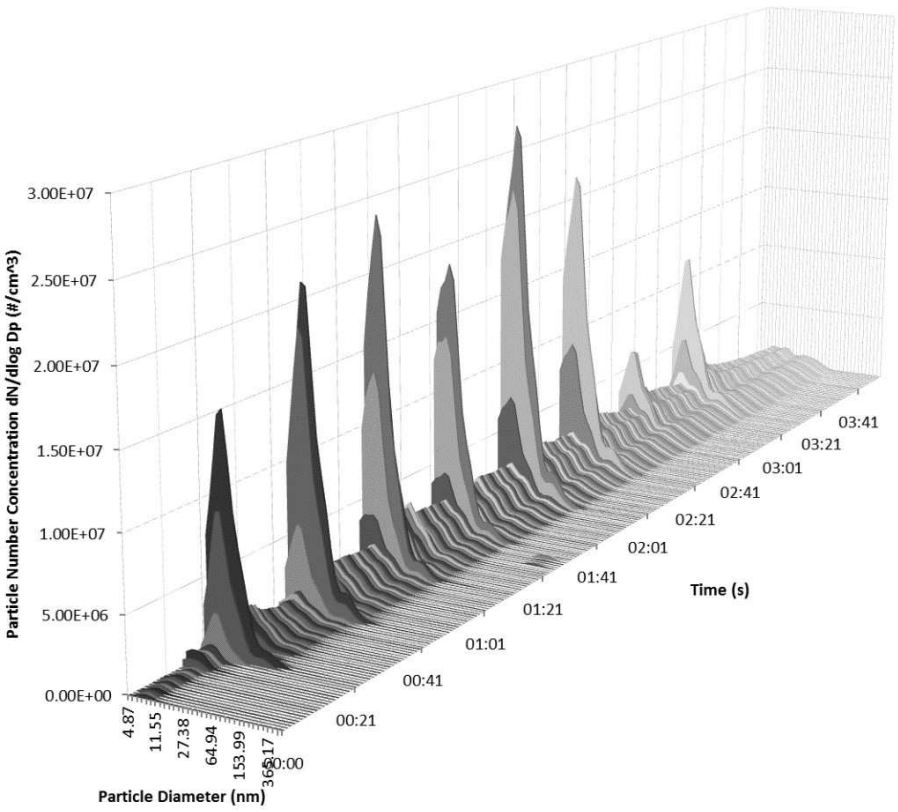

Figure 6: Size distribution during 4 minutes for EP/CNT sample recorded on DMS50

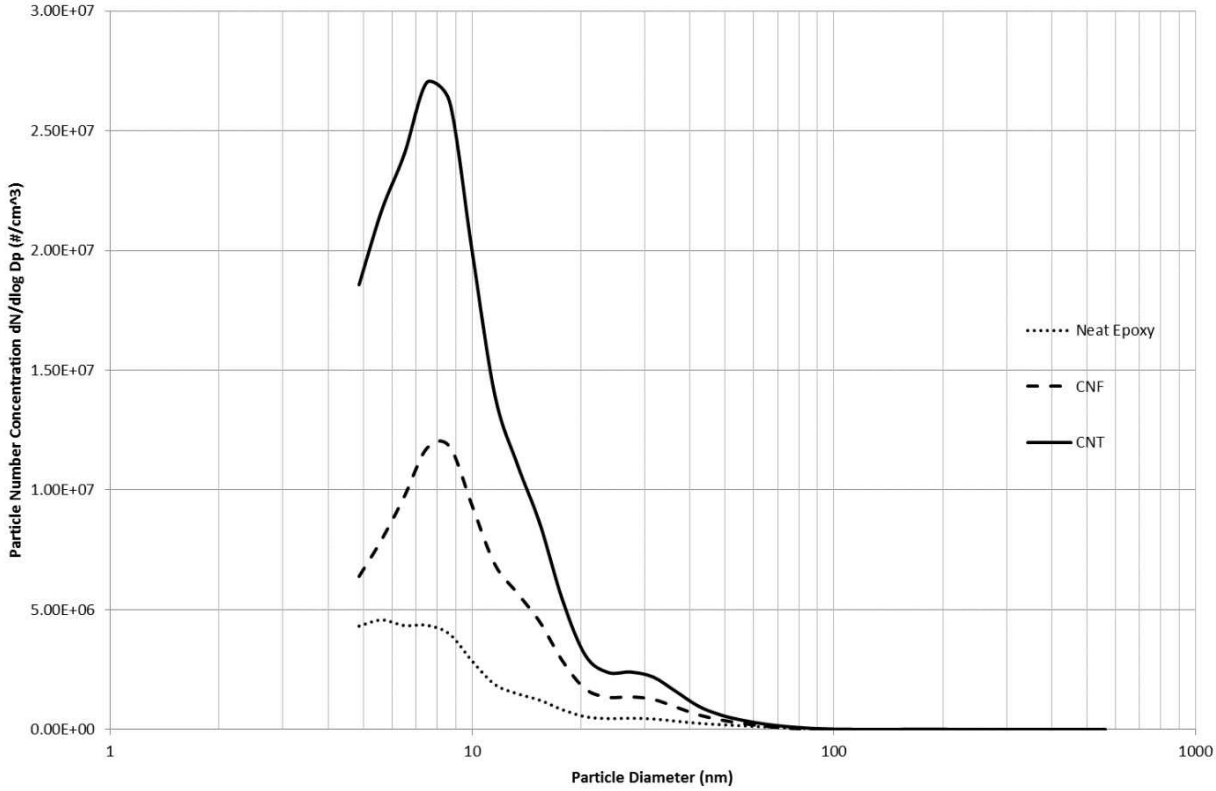

Figure 7: Peak particle size distribution within the 4 minutes sampling of the epoxy-based samples recorded on DMS50

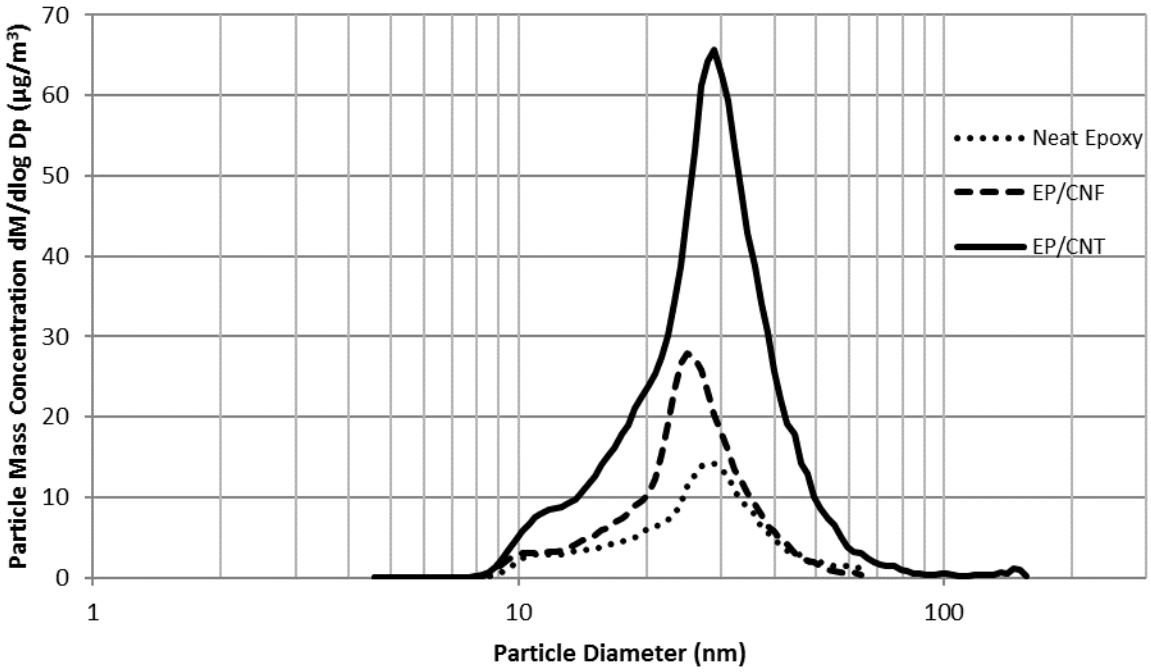

Figure 8: Particle mass concentration average over 4 minutes of epoxy based nanocomposites determined from SMPS

Figure 9: SEM images of collected debris from sampling tray within chamber of Neat Epoxy (left), EP/CNF (middle) and EP/CNT (right) samples

Table 1: Numerical values of particle number concentration during drilling (Note: CPC limit of 9.99 x 10^6 #/cm^3 and the mean peaks therefore represent a lower bound value that include the saturated peaks. Mean values over 4 min and percentage mean increase from neat epoxy exclude the saturated peaks)

	Mean Peak Value $\bar{X}$ [x 10^6 #/cm^3]	**Mean Peak Deviation S_X [x 10^6 #/cm^3]**	**Minimum Peak [x 10^6 #/cm^3]**	**Maximum Peak [x 10^6 #/cm^3]**	**Concentration after 4th Min [x 10^6 #/cm^3]**	**Mean over 4 min [x 10^6 #/cm^3]**	**Percentage mean increase from Neat Epoxy**
EP	>4.06	>3.87	0.81	>9.99	0.513	0.454	N/A
EP/CNT	>8.56	>3.44	6.61	>9.99	1.01	1.48	227%
EP/CNF	>7.59	>1.17	1.62	>9.99	0.785	0.915	102%